# Electronic Supplementary Information

## A series of complexes based on biphenyl-2,5,2′,5′-tetracarboxylic acid: syntheses, crystal structures, luminescent and magnetic properties

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**Table S1.** Selected bond lengths/Å and angles/° for complexes **1**−**5**.

| | | | | | |
|---|---|---|---|---|---|
| **{[$Cu_2$(bptc)($H_2O$)$_6$]·11$H_2O$}$_n$ (1)** | | | | | |
| Cu1–O1W | 1.955(3) | Cu1–O3A | 1.957(2) | Cu1–O2W | 1.962(3) |
| Cu1–O1 | 1.967(2) | Cu1–O3W | 2.279(4) | O3A–Cu1–O1W | 90.71(11) |
| O2W–Cu1–O1W | 175.88(13) | O2W–Cu1–O3A | 86.78(11) | O1–Cu1–O1W | 87.90(10) |
| O1–Cu1–O3A | 172.64(11) | O1–Cu1–O2W | 94.17(11) | O3W–Cu1–O1W | 88.36(14) |
| O3W–Cu1–O3A | 97.24(13) | O3W–Cu1–O2W | 95.19(16) | O3W–Cu1–O1 | 89.94(13) |
| **{[$Ni_2$(bptc)($H_2O$)$_6$]·11$H_2O$}$_n$ (2)** | | | | | |
| Ni1–O1W | 1.955(2) | Ni1–O3A | 1.957(2) | Ni1–O2W | 1.965(2) |
| Ni1–O1 | 1.966(2) | Ni1–O3W | 2.280(3) | O3A–Ni1–O1W | 90.95(10) |
| O2W–Ni1–O1W | 175.91(12) | O2W–Ni1–O3A | 86.48(10) | O1–Ni1–O1W | 87.99(9) |
| O1–Ni1–O3A | 172.91(11) | O1–Ni1–O2W | 94.16(10) | O3W–Ni1–O1W | 88.38(12) |
| O3W–Ni1–O3A | 97.16(12) | O3W–Ni1–O2W | 95.10(13) | O3W–Ni1–O1 | 89.83(12) |
| **{[$Co_2$($H_2$bptc)$_2$(4,4′-bpy)$_2$($H_2O$)$_2$]·4$H_2O$}$_n$ (3)** | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Co1–O1W | 2.072(2) | Co1–O1WC | 2.072(2) | Co1–O1C | 2.093(2) |
| Co1–O1 | 2.093(2) | Co1–N1 | 2.144(3) | Co1–N2D | 2.165(4) |
| Co2–O2B | 2.0560(2) | Co2–O2 | 2.0560(2) | Co2–N3 | 2.124(4) |
| Co2–N4 | 2.186(4) | Co2–O7 | 2.235(2) | Co2–O7B | 2.235(2) |
| O1W–Co1–O1WC | 175.78(12) | O1W–Co1–O1C | 96.97(8) | O1WC–Co1–O1C | 82.79(8) |
| O1W–Co1–O1 | 82.79(8) | O1WC–Co1–O1 | 96.97(8) | O1C–Co1–O1 | 173.44(12) |
| O1W–Co1–N1 | 92.11(6) | O1WC–Co1–N1 | 92.11(6) | O1C–Co1–N1 | 93.28(6) |
| O1–Co1–N1 | 93.28(6) | O1W–Co1–N2D | 87.89(6) | O1WC–Co1–N2D | 87.89(6) |
| O1C–Co1–N2D | 86.72(6) | O1–Co1–N2D | 86.72(6) | N1–Co1–N2D | 180.0 |
| O2–Co2–O2B | 177.30(12) | O2–Co2–N3 | 91.35(6) | O2B–Co2–N3 | 91.35(6) |
| O2–Co2–N4 | 88.65(6) | O2B–Co2–N4 | 88.65(6) | N3–Co2–N4 | 180.0 |
| O2B–Co2–O7B | 97.90(8) | O2–Co2–O7B | 82.26(8) | N3–Co2–O7B | 86.62(5) |
| N4–Co2–O7B | 93.38(5) | O2–Co2–O7 | 82.26(8) | O2B–Co2–O7 | 97.90(8) |
| N3–Co2–O7 | 86.62(5) | N4–Co2–O7 | 93.38(5) | O7B–Co2–O7 | 173.24(11) |

**$[Ni_2(bptc)(2,2'\text{-bpy})_2(H_2O)_6]\cdot 2H_2O$ (4)**

| | | | | | |
|---|---|---|---|---|---|
| Ni1–N1 | 2.072(4) | Ni1–N2 | 2.048(4) | Ni2–N3 | 2.046(4) |
| Ni2–N4 | 2.076(4) | Ni1–O1 | 2.031(3) | Ni1–O2W | 2.064(3) |
| Ni1–O1W | 2.084(3) | Ni1–O3W | 2.107(3) | Ni2–O5 | 2.051(3) |
| Ni2–O5W | 2.070(3) | Ni2–O6W | 2.063(3) | Ni2–O4W | 2.083(3) |
| O1–Ni1–N2 | 90.78(14) | O1–Ni1–O2W | 93.64(12) | N2–Ni1–O2W | 175.49(15) |
| O1–Ni1–N1 | 169.94(15) | N2–Ni1–N1 | 79.28(16) | O2W–Ni1–N1 | 96.27(15) |
| O1–Ni1–O1W | 89.65(13) | N2–Ni1–O1W | 90.88(14) | O2W–Ni1–O1W | 88.30(12) |

| | | | | | |
|---|---|---|---|---|---|
| N1–Ni1–O1W | 88.94(15) | O1–Ni1–O3W | 87.64(12) | N2–Ni1–O3W | 90.23(14) |
| O2W–Ni1–O3W | 90.80(12) | N1–Ni1–O3W | 93.91(14) | O1W–Ni1–O3W | 177.09(13) |
| N3–Ni2–O5 | 89.41(14) | N3–Ni2–O5W | 173.61(15) | O5–Ni2–O5W | 93.81(12) |
| N3–Ni2–O6W | 89.70(14) | O5–Ni2–O6W | 90.27(14) | O5W–Ni2–O6W | 84.77(13) |
| N3–Ni2–N4 | 79.08(17) | O5–Ni2–N4 | 168.49(15) | O5W–Ni2–N4 | 97.61(16) |
| O6W–Ni2–N4 | 89.32(15) | N3–Ni2–O4W | 92.40(14) | O5–Ni2–O4W | 89.57(13) |
| O5W–Ni2–O4W | 93.14(13) | O6W–Ni2–O4W | 177.89(13) | N4–Ni2–O4W | 91.25(14) |

**$[Zn_2(bptc)(2,2'\text{-bpy})_2(H_2O)_6]\cdot 3H_2O$ (5)**

| | | | | | |
|---|---|---|---|---|---|
| Zn1–O1 | 2.054(4) | Zn1–O2W | 2.075(4) | Zn1–N2 | 2.106(5) |
| Zn1–O3W | 2.184(5) | Zn1–N1 | 2.158(5) | Zn1–O1W | 2.133(5) |
| Zn2–O5 | 2.070(4) | Zn2–O6W | 2.133(4) | Zn2–N3 | 2.119(5) |
| Zn2–O5W | 2.101(4) | Zn2–O4W | 2.138(4) | Zn2–N4 | 2.159(5) |
| O1–Zn1–O2W | 94.60(17) | O1–Zn1–N2 | 90.42(18) | O2W–Zn1–N2 | 174.98(19) |
| O1–Zn1–O3W | 88.31(16) | O2W–Zn1–O3W | 89.0(2) | N2–Zn1–O3W | 91.37(19) |
| O1–Zn1–N1 | 167.58(19) | O2W–Zn1–N1 | 97.7(2) | N2–Zn1–N1 | 77.3(2) |
| O3W–Zn1–N1 | 93.73(18) | O1–Zn1–O1W | 90.52(18) | O2W–Zn1–O1W | 88.3(2) |
| N2–Zn1–O1W | 91.43(19) | O3W–Zn1–O1W | 176.97(18) | N1–Zn1–O1W | 88.00(19) |
| O5–Zn2–O5W | 95.50(16) | O5–Zn2–N3 | 88.95(18) | O5–Zn2–N4 | 166.0(2) |
| O6W–Zn2–O5 | 91.14(18) | O6W–Zn2–O5W | 83.19(16) | N3–Zn2–O5W | 171.47(19) |
| O6W–Zn2–N3 | 89.45(18) | O6W–Zn2–O4W | 175.43(16) | N3–Zn2–O4W | 95.11(18) |
| O5W–Zn2–O4W | 92.24(17) | O5–Zn2–O4W | 89.22(16) | O6W–Zn2–N4 | 89.25(19) |
| N3–Zn2–N4 | 77.1(2) | O5W–Zn2–N4 | 98.40(19) | O4W–Zn2–N4 | 91.50(18) |

a Symmetry codes: A: *x*–1/2, *y*+1/2, *z*; B: –*x*+3/2, *y*, –*z*+1/2; C: –*x*+5/2, *y*, –*z*+1/2; D: *x*, *y*–1, *z*.

**Table S2.** O–H···O, C–H···O, C–H···π and π···π interactions for **1**−**5**.

| D–H···A | D–H(Å) | H···A(Å) | D···A(Å) | □DHA (°) | Symmetry codes |
|---|---|---|---|---|---|
| **{[$Cu_2$(bptc)($H_2O$)$_6$]·11$H_2O$}$_n$ (1)** | | | | | |
| O1W–H1WB···O2 | 0.85 | 1.94 | 2.713(4) | 151 | −*x*+1/2, −*y*+1/2, −*z*+1 |
| O1W–H1WA···O4 | 0.85 | 1.82 | 2.657(5) | 167 | −*x*, −*y*+1, −*z*+1 |
| O3W–H3WA···O5W | 0.82 | 2.16 | 2.836(6) | 140 | |
| O2W–H2WB···O4W | 0.85 | 1.88 | 2.716(5) | 168 | |
| O4W–H4WB···O6W | 0.85 | 1.95 | 2.779(6) | 163 | |
| O4W–H4WA···O5W | 0.85 | 1.96 | 2.793(6) | 167 | −*x*+1/2, −*y*+1/2, −*z* |
| O5W–H5WB···O3W | 0.82 | 2.32 | 2.836(6) | 122 | |
| O5W–H5WB···O8W | 0.82 | 2.38 | 2.720(14) | 106 | |
| O5W–H5WA···O8W | 0.82 | 2.34 | 2.720(14) | 109 | |
| O6W–H6WB···O3 | 0.85 | 2.00 | 2.808(5) | 160 | −*x*+1/2, *y*−1/2, −*z*+1/2 |
| O6W–H6WA···O5W | 0.86 | 1.92 | 2.725(6) | 156 | |
| O7W–H7WA···O2W | 0.82 | 2.34 | 3.106(6) | 157 | −*x*, *y*, −*z*+1/2 |
| O7W–H7WB···O8W | 0.82 | 2.34 | 2.744(13) | 111 | −*x*+1/2, *y*−1/2, −*z*+1/2 |
| O8W–H8WA···O9W | 0.82 | 2.23 | 2.810(18) | 128 | *x*+1/2,–*y*+1/2, *z*–1/2 |
| O9W–H9WA···O4W | 0.82 | 1.97 | 2.770(6) | 166 | *x*, −*y*, *z*+1/2 |
| O9W–H9WB···O1 | 0.82 | 2.37 | 2.963(6) | 129 | −*x*+1/2, −*y*+1/2, −*z*+1 |
| **{[$Ni_2$(bptc)($H_2O$)$_6$]·11$H_2O$}$_n$ (2)** | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O2W–H2WB···O4W | 0.84 | 1.88 | 2.708(4) | 168 | |
| O1W–H1WA···O4 | 0.85 | 1.83 | 2.660(4) | 167 | −*x*, −*y*+1, −*z*+1 |
| O1W–H1WB···O2 | 0.84 | 1.94 | 2.703(3) | 151 | −*x*+1/2, −*y*+1/2, −*z*+1 |
| O3W–H3WA···O5W | 0.81 | 2.15 | 2.837(6) | 142 | |
| O4W–H4WB···O6W | 0.85 | 1.95 | 2.776(5) | 163 | |
| O4W–H4WA···O5W | 0.85 | 1.95 | 2.785(5) | 167 | −*x*+1/2, −*y*+1/2, −*z* |
| O6W–H6WB···O3 | 0.85 | 2.01 | 2.818(5) | 160 | −*x*+1/2, *y*−1/2, −*z*+1/2 |
| O6W–H6WA···O5W | 0.87 | 1.89 | 2.712(5) | 157 | |
| O7W–H7WA···O2W | 0.82 | 2.33 | 3.105(6) | 157 | −*x*, *y*, −*z*+1/2 |
| O7W–H7WB···O8W | 0.82 | 2.37 | 2.763(11) | 110 | −*x*+1/2, *y* −1/2,−*z*+1/2 |
| O8W–H8WA···O9W | 0.82 | 2.19 | 2.778(14) | 128 | *x*+1/2, −*y*+1/2, *z*−1/2 |
| O9W–H9WA···O4W | 0.82 | 1.97 | 2.776(5) | 166 | *x*, −*y*,1/2+*z* |
| O9W–H9WB···O1 | 0.82 | 2.37 | 2.962(5) | 130 | −*x*+1/2,−*y*+1/2,−*z*+1 |
| O5W–H5WA···O8W | 0.84 | 2.32 | 2.718(11) | 110 | |
| O5W–H5WB···O3W | 0.82 | 2.33 | 2.837(6) | 120 | |
| O5W–H5WB···O8W | 0.82 | 2.35 | 2.718(11) | 108 | |

**{[$Co_2(H_2bptc)_2$(4,4′-bpy)$_2(H_2O)_2$]·4$H_2O$}$_n$ (3)**

| | | | | | |
|---|---|---|---|---|---|
| O1W–H1WA···O4 | 0.82 | 2.01 | 2.795(3) | 159 | –*x*+1, –*y*, –*z* |
| O1W–H1WB···O7 | 0.83 | 1.81 | 2.634(3) | 171 | *x*–1, *y*, *z* |
| O3–H3···O8 | 0.82 | 1.93 | 2.727(4) | 163 | –*x*+2, –*y*, –*z* |
| O3W–H3WA···O8 | 0.82 | 1.99 | 2.800(4) | 167 | –*x*+1,–*y*+1, –*z* |
| O3W–H3WB···O3W | 0.82 | 2.12 | 2.855(5) | 150 | –*x*, –*y*+1, –*z* |

| | | | | | |
|---|---|---|---|---|---|
| O5–H5···O3W | 0.82 | 1.85 | 2.658(5) | 169 | |
| O2W–H2WA···O3W | 0.82 | 2.20 | 2.771(9) | 127 | *x*+1, *y*, *z* |
| π···π [a] | | | 3.870(2) | | –*x*+1, –*y*, –*z* |
| **[$Ni_2$(bptc)(2,2′-bpy)$_2$($H_2O$)$_6$]·2$H_2O$ (4)** | | | | | |
| O3W–H3WA···O7 | 0.89 | 1.87 | 2.712(5) | 157 | –*x*+2, *y*–1/2, –*z*+1/2 |
| O1W–H1WA···O7 | 0.82 | 1.99 | 2.792(5) | 165 | –*x*+2, –*y*+1, –*z*+1 |
| O1W–H1WB···O6 | 0.81 | 1.96 | 2.746(5) | 164 | *x*,–*y*+1/2, *z*+1/2 |
| O6W–H6WB···O2 | 0.78 | 2.07 | 2.826(5) | 163 | *x*,–*y*+1/2, *z*–1/2 |
| O6W–H6WA···O4 | 0.74 | 1.86 | 2.596(7) | 171 | –*x*+1, –*y*+1, –*z* |
| O2W–H2WA···O8 | 0.88 | 1.91 | 2.737(5) | 157 | –*x*+2, *y*–1/2, –*z*+1/2 |
| O8W–H8WA···O3 | 0.82 | 2.59 | 3.407(18) | 173 | –*x*+1, *y*–1/2, –*z*+1/2 |
| O7W–H7WA···O3 | 0.86 | 2.40 | 2.798(9) | 109 | –*x*+1, *y*–1/2, –*z*+1/2 |
| O7W–H7WB···O8 | 0.85 | 2.59 | 2.873(7) | 101 | –*x*+2, *y*–1/2, –*z*+1/2 |
| O5W–H5WA···O7W | 0.82 | 1.96 | 2.775(5) | 177 | |
| O4W–H4WA···O3 | 0.82 | 1.97 | 2.772(5) | 168 | –*x*+1, *y*–1/2, –*z*+1/2 |
| C30–H30···O7 | 0.93 | 2.60 | 3.480(7) | 158 | –*x*+1, –*y*+1, –*z* |
| C35–H35···O7W | 0.93 | 2.43 | 3.313(9) | 157 | –*x*+1, –*y*, –*z* |
| C29–H29···π [b] | 0.93 | 2.79 | 3.607(6) | 147 | –*x*+1, –*y*+1, –*z* |
| C8–H8···π [c] | 0.93 | 2.63 | 3.250(6) | 125 | –*x*+2, –*y*+1, –*z*+1 |
| π···π [d] | | | 3.789(3) | | *x*+1,–*y*+1/2, *z*+1/2 |
| π···π [e] | | | 3.939(4) | | *x*+1,–*y*+1/2, *z*+1/2 |
| **[$Zn_2$(bptc)(2,2′-bpy)$_2$($H_2O$)$_6$]·3$H_2O$ (5)** | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| O6W–H6WB···O2 | 0.79 | 2.06 | 2.825(7) | 164 | *x*, −*y*+1/2, *z*−1/2 |
| O5W–H5WA···O7W | 0.83 | 1.92 | 2.750(7) | 179 | |
| O8W–H8WA···O3 | 0.82 | 2.40 | 3.18(2) | 159 | −*x*+1, *y*−1/2, −*z*+1/2 |
| O8W–H8WB···O2W | 0.83 | 2.46 | 3.072(18) | 132 | |
| O8W–H8WB···O9W | 0.83 | 1.93 | 2.48(3) | 123 | −*x*+1, *y*−1/2, −*z*+1/2 |
| O9W–H9WA···O8 | 0.84 | 1.86 | 2.699(18) | 176 | *x*−1, *y*, *z* |
| O6W–H6WA···O4 | 0.75 | 1.88 | 2.619(8) | 172 | −*x*+1, −*y*+1, −*z* |
| O3W–H3WA···O7 | 0.90 | 1.94 | 2.784(7) | 154 | −*x*+2, *y*−1/2, −*z*+1/2 |
| O3W–H3WA···O8 | 0.90 | 2.54 | 3.302(6) | 143 | −*x*+2, *y*−1/2, −*z*+1/2 |
| O1W–H1WA···O7 | 0.83 | 1.97 | 2.794(8) | 171 | −*x*+2, −*y*+1, −*z*+1 |
| O1W–H1WB···O6 | 0.82 | 2.00 | 2.788(7) | 163 | *x*, −*y*+1/2, *z*+1/2 |
| O4W–H4WA···O3 | 0.83 | 1.98 | 2.794(7) | 167 | −*x*+1, *y*−1/2, −*z*+1/2 |
| O2W–H2WA···O8 | 0.89 | 2.08 | 2.927(7) | 158 | −*x*+2, *y*−1/2, −*z*+1/2 |
| O2W–H2WA···O9W | 0.89 | 2.54 | 2.986(18) | 112 | −*x*+1, *y*−1/2, −*z*+1/2 |
| O7W–H7WA···O3 | 0.76 | 2.38 | 2.782(11) | 114 | −*x*+1, *y*−1/2, −*z*+1/2 |
| O7W–H7WB···O8 | 0.83 | 2.55 | 2.960(9) | 111 | −*x*+2, *y*−1/2, −*z*+1/2 |
| C23–H23···O9W | 0.93 | 2.55 | 3.335(19) | 143 | *x*+1, *y*, *z* |
| C35–H35···O7W | 0.93 | 2.46 | 3.380(11) | 168 | −*x*+1, −*y*, −*z* |
| C29–H29···π [b] | 0.93 | 2.82 | 3.616(8) | 144 | −*x*+1, −*y*+1, −*z* |
| C8–H8···π [c] | 0.93 | 2.65 | 3.293(9) | 144 | −*x*+2, −*y*+1, −*z*+1 |
| π···π [d] | | | 3.815(5) | | *x*+1,–*y*+1/2, *z*+1/2 |
| π···π [e] | | | 3.926(5) | | *x*+1,–*y*+1/2, *z*+1/2 |

a Centroid C2–C3–C4–C5–C6–C7 and C2–C3–C4–C5–C6–C7.

b Centroid C19–C20–C21–C23–C24–C25.

c Centroid C12–C13–C14–C15–C17–C18.

d Centroids N3–C27–C28–C29–C30–C31 and N1–C1–C2–C3–C4–C5.

e Centroids N2–C6–C7–C8–C9–C10 and N4–C32–C33–C34–C35–C36.

**Table S3.** The dihedral angles for $H_2bptc^{2-}$ and $bptc^{4-}$ ligands in **1**−**5**.

| Dihedral angles between carboxylate groups and correspondingly linking phenyl rings | | | | |
|---|---|---|---|---|
| | 2-carboxylic group | 5-carboxylic group | 2′-carboxylic group | 5′-carboxylic group |
| **1** | 34.13˚ | 23.80˚ | 34.13˚ | 23.80˚ |
| **2** | 33.84˚ | 23.29˚ | 33.84˚ | 23.29˚ |
| **3** | 50.67˚ | 8.21˚ | 62.13˚ | 0.65˚ |
| **4** | 35.22˚ | 20.47˚ | 35.72˚ | 9.72˚ |
| **5** | 36.73˚ | 15.84˚ | 34.63˚ | 8.83˚ |

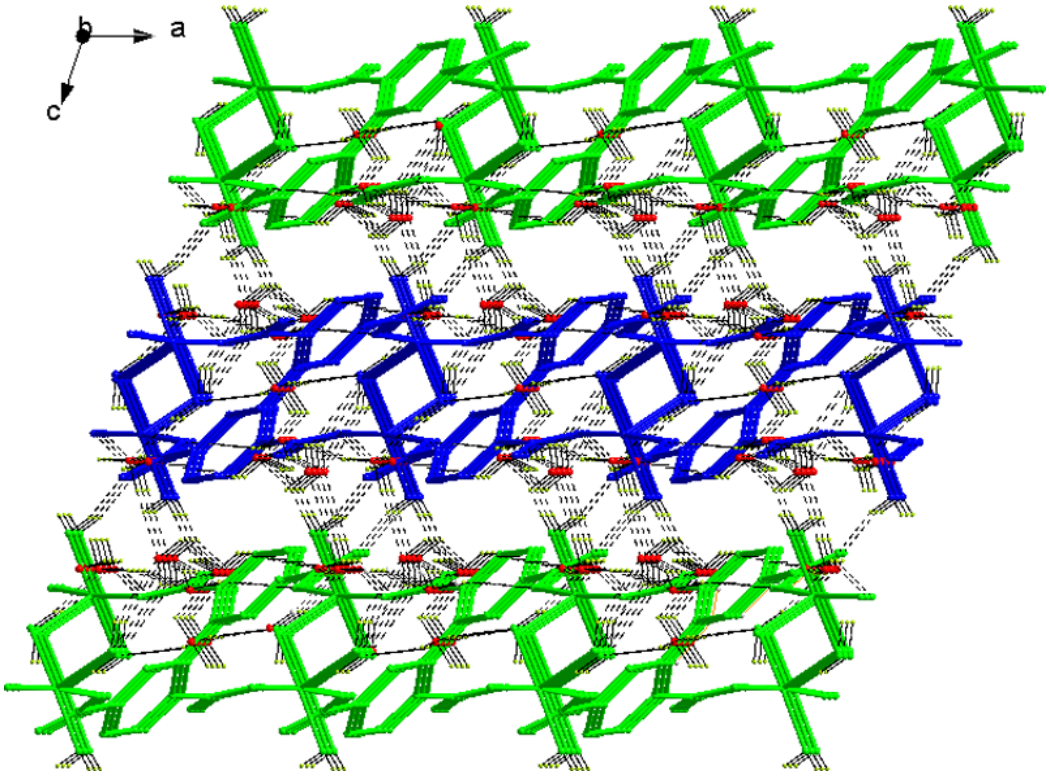



**Fig. S1.** Perspective view of the 3D structure formed via intermolecular O–H···O interactions viewed along the *b* axis in **1**.

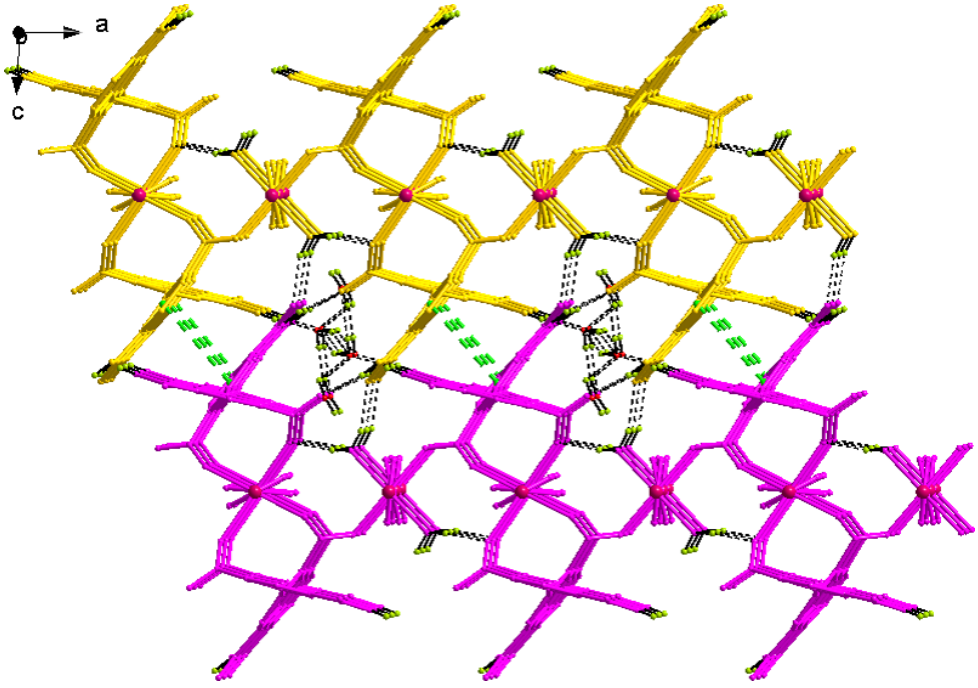



**Fig. S2.** The 3D structure formed via intermolecular O–H···O (black dotted lines) and π···π (bright green dotted lines) stacking interactions viewed along the *b* axis in **3**.

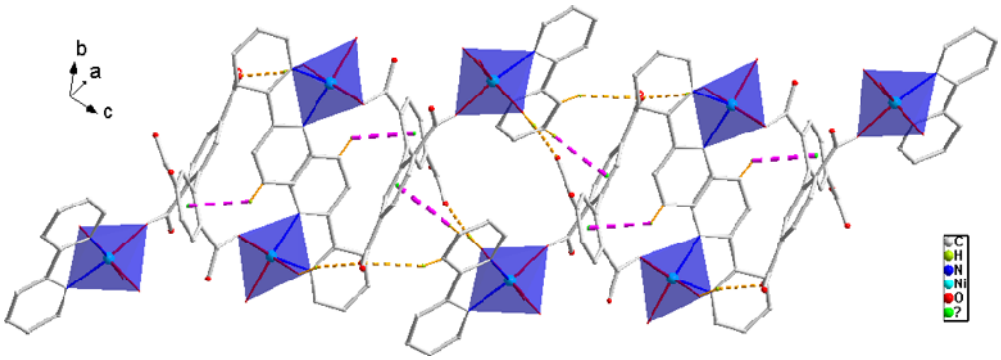
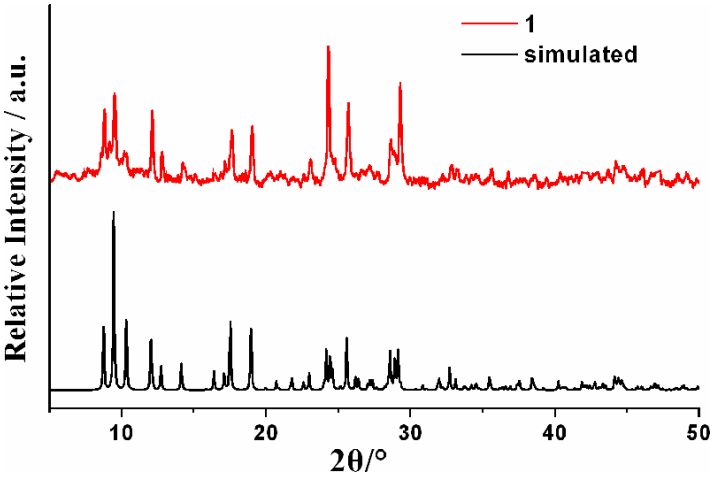
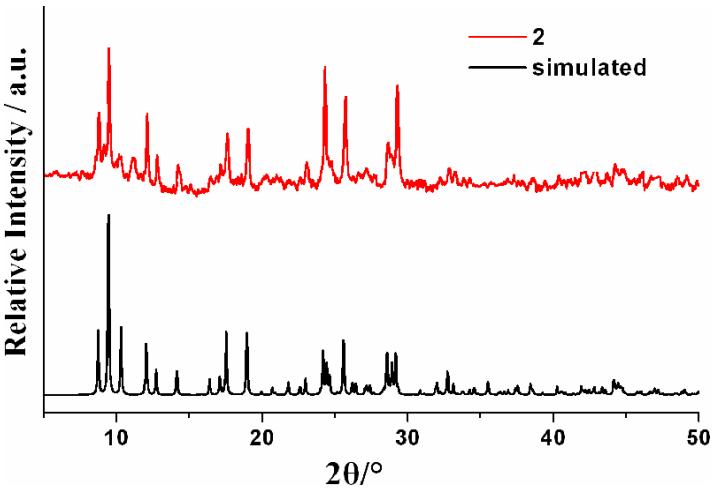



**Fig. S3.** Polyhedral view of the infinite 1D double chains formed by intermolecular O–H···O, C–H···O (light orange dotted lines) and C–H···$\pi$ (pink dotted lines) interactions in **4**.



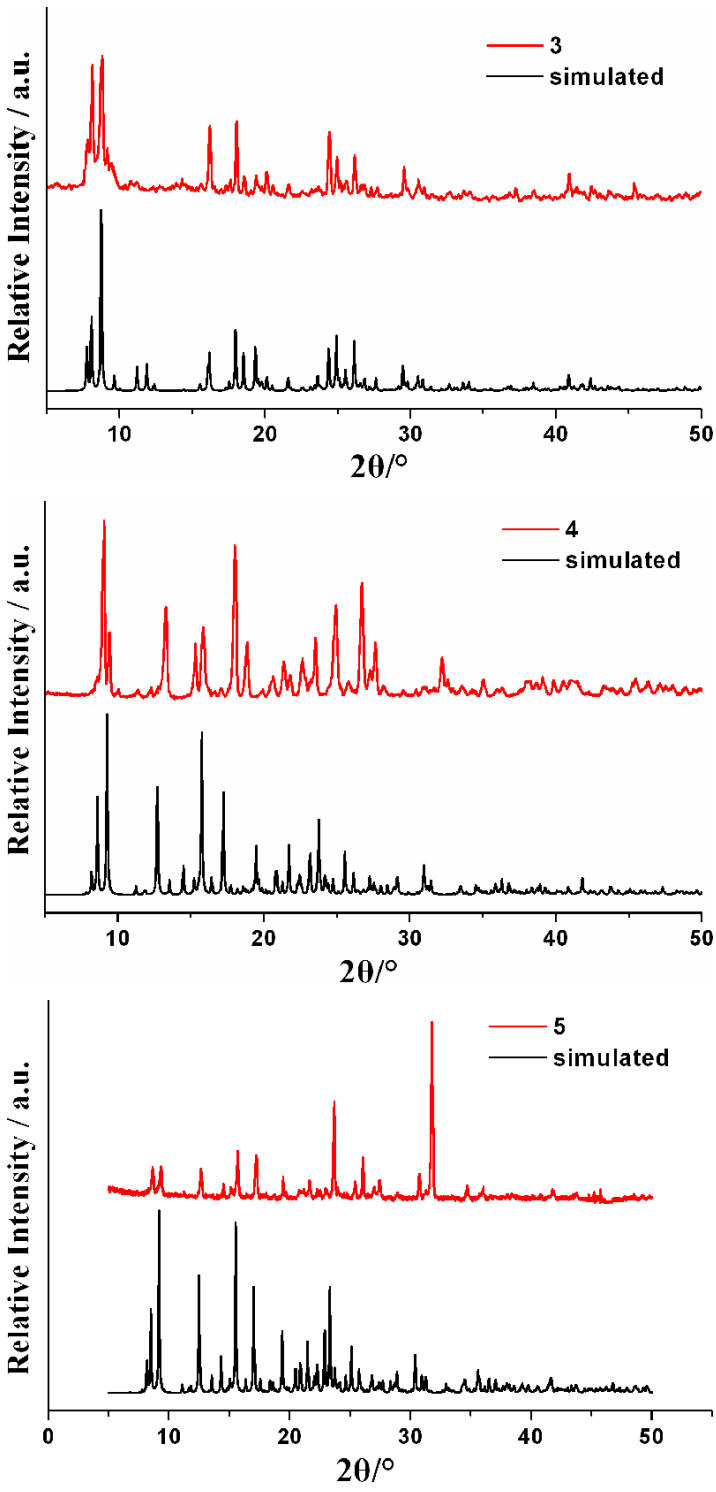



**Fig. S4** The XRPD patterns for complexes **1**−**5**: the as-synthesized patterns (red) and the simulated based on X-ray single-crystal data (black).

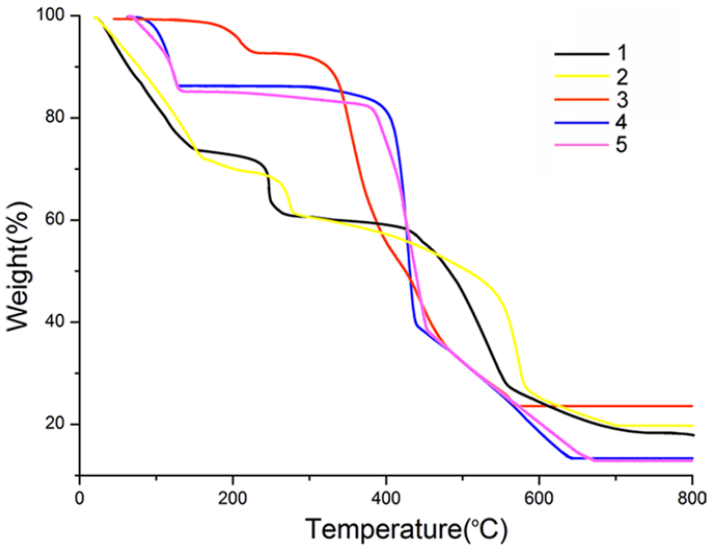



**Fig. S5.** Thermogravimetric curves of complexes **1**−**5**.

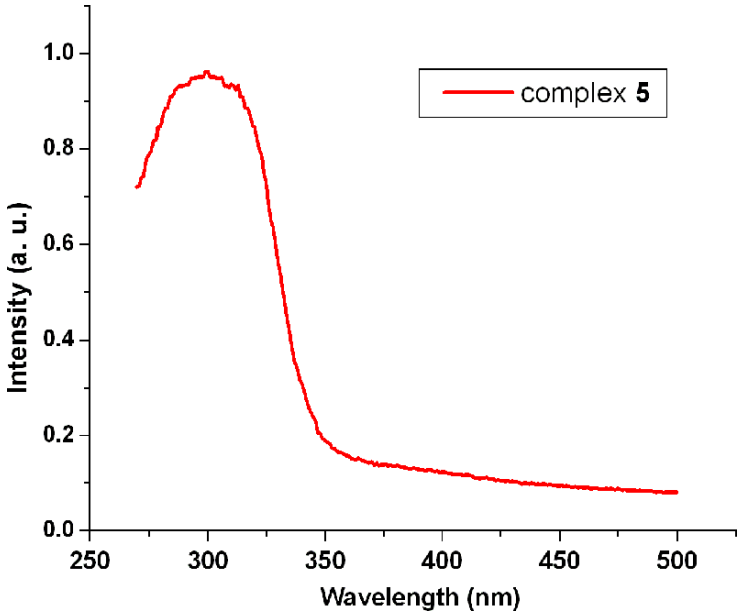



**Fig. S6.** The UV-vis spectra of complex **5** at room temperature in the solid state.

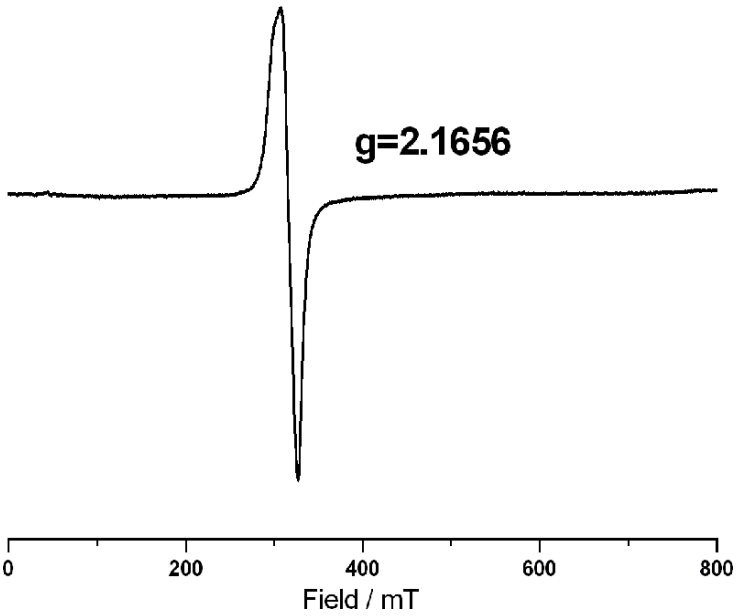



**Fig. S7.** Room-temperature X-band EPR spectra of complex **1** at room temperature under argon.

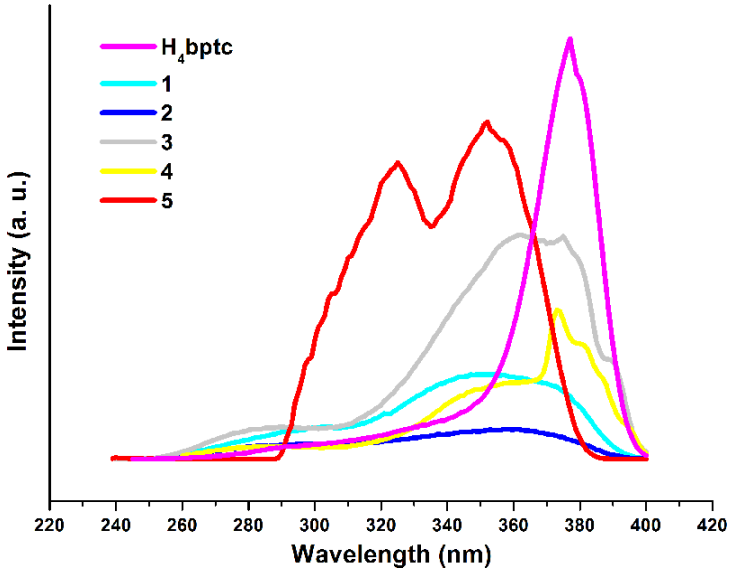



**Fig. S8.** The excitation spectras of **1**−**5** and $H_4$bptc ligand at room temperature.

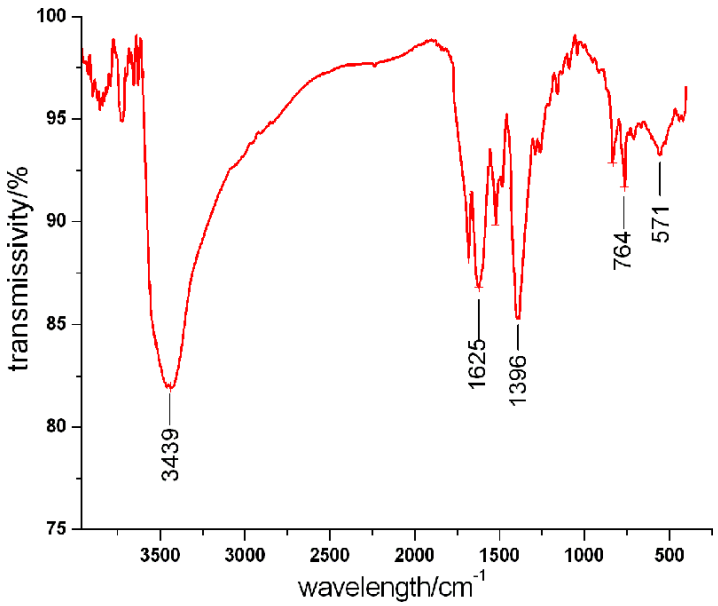



**Fig. S9.** IR spectrum of complex **1**.

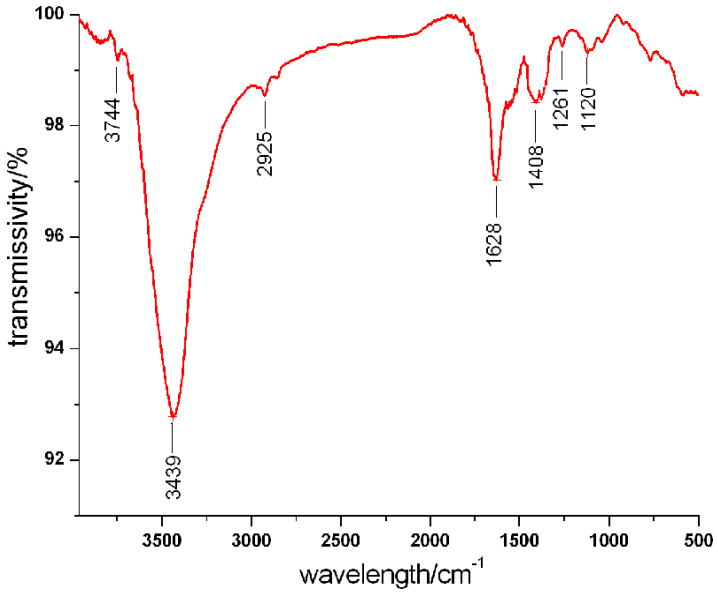



**Fig. S10.** IR spectrum of complex **2**.

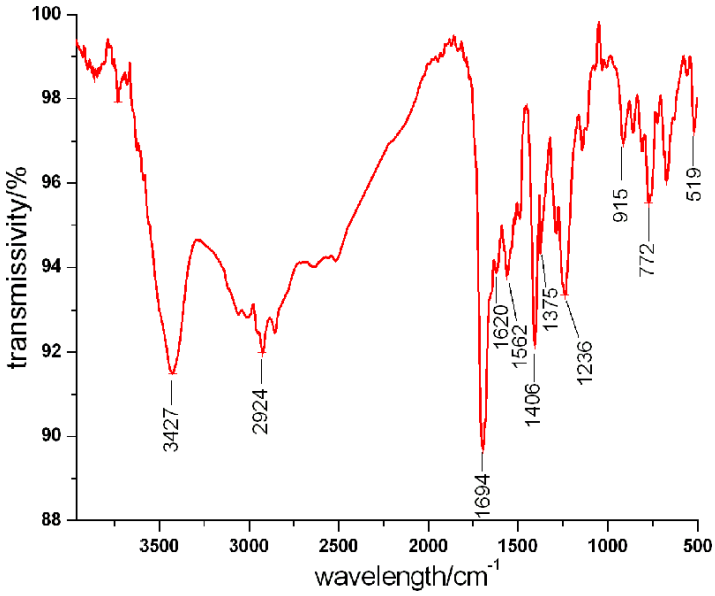



**Fig. S11.** IR spectrum of complex **3**.

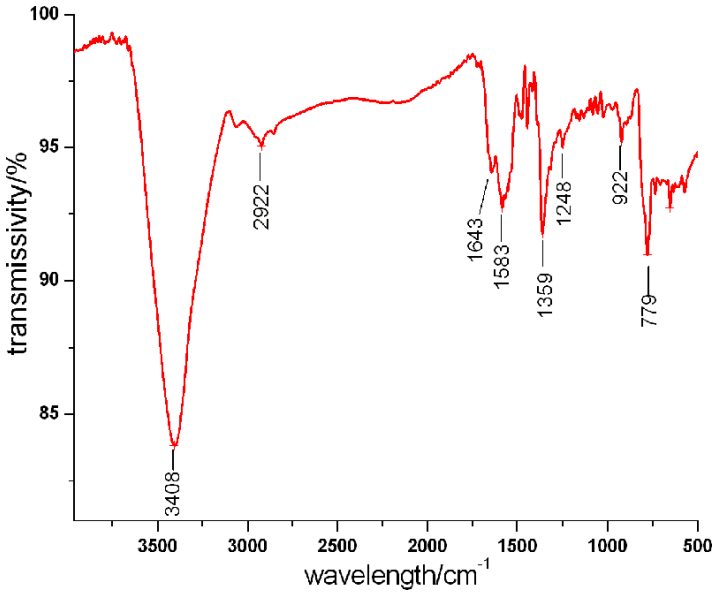



**Fig. S12.** IR spectrum of complex **4**.

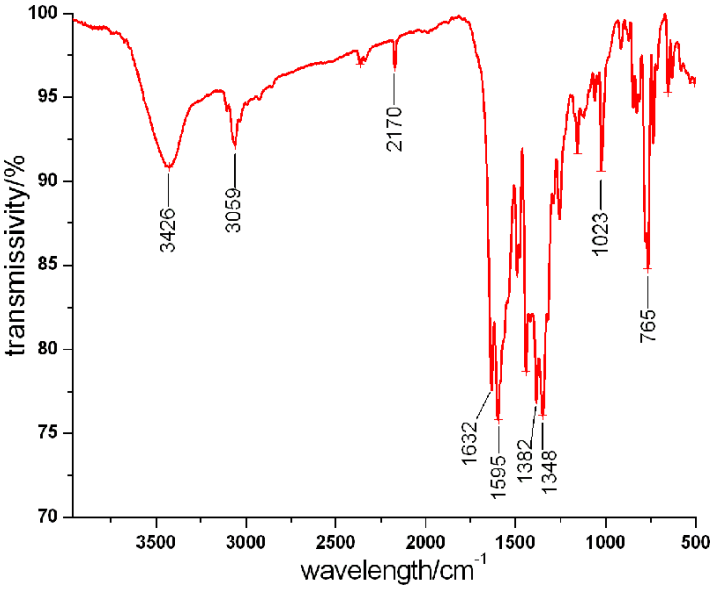



**Fig. S13.** IR spectrum of complex **5**.